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(54) **STEEL SHEET FOR HIGH-STRENGTH LINE PIPE HAVING EXCELLENT LOW TEMPERATURE TOUGHNESS, AND STEEL TUBE FOR HIGH-STRENGTH LINE PIPE**

STAHLBLECH FÜR HOCHFESTES LEITUNGSROHR MIT HERVORRAGENDER TIEFTEMPERATURZÄHIGKEIT UND STAHLROHR FÜR HOCHFESTES LEITUNGSROHR

TÔLE D'ACIER POUR TUYAU DE CANALISATION À HAUTE RÉSISTANCE AYANT UNE EXCELLENTE TÉNACITÉ À BASSE TEMPÉRATURE ET TUBE EN ACIER POUR TUYAU DE CANALISATION À HAUTE RÉSISTANCE

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(73) Proprietor: **Kabushiki Kaisha Kobe Seiko Sho (Kobe Steel, Ltd.)**

**Kobe-shi, Hyogo 651-8585 (JP)**

(72) Inventors:

- **KOBAYASHI, Yoshiyuki**  
**Kobe-shi**  
**Hyogo 651-2271 (JP)**

- **KAWANO, Haruya**  
**Hyogo 675-0137 (JP)**

(74) Representative: **Müller-Boré & Partner**

**Patentanwälte PartG mbB**  
**Friedenheimer Brücke 21**  
**80639 München (DE)**

(56) References cited:

**EP-A1- 2 980 238      EP-A1- 3 018 231**  
**JP-A- H0 920 921      JP-A- H1 171 615**  
**JP-A- 2003 064 418      JP-A- 2003 096 517**  
**JP-A- 2011 106 012      JP-A- 2012 072 472**  
**JP-A- 2012 126 925      JP-A- 2013 213 242**

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**Description**

5 **[0001]** The present invention relates to a steel plate for a high-strength line pipe and to a steel tube for a high-strength line pipe manufactured from the steel plate for a high-strength line pipe. In detail, the present invention relates to a steel plate for a high-strength line pipe having an excellent critical CTOD (Crack Tip Opening Displacement) value and to a steel tube for a high-strength line pipe.

10 **[0002]** Line pipes used for transportation of natural gas and oil tend to undergo high pressure as an operating pressure for the purpose of improving the transportation efficiency. Steel plates for such line pipes are required to have higher strength. Additionally, in terms of safety, steel plates are required to exhibit excellent CTOD properties in a CTOD test, which is an assessment index of fracture toughness as a characteristics of brittle fracture occurrence prevention.

15 **[0003]** To strengthen steel, some strengthening mechanisms of steel materials have been proposed, including solid solution strengthening, precipitation hardening, transformation hardening, and dislocation strengthening. Among them, the dislocation strengthening, which involves strengthening the material by increasing the dislocation density, can be exhibited by increasing a cumulative rolling reduction ratio in the so-called dual-phase temperature range, where part of an austenite single-phase microstructure is transformed into ferrite in a rolling step of the manufacturing procedure of a steel plate. Thus, the dislocation strengthening mechanism can be applied more easily, compared to other strengthening mechanisms.

20 **[0004]** However, increasing the cumulative rolling reduction ratio in the dual-phase temperature range causes the rotation of crystal orientation together with the increase in dislocation density, developing a texture. Such development of the texture leads to a large difference in the toughness of the steel between the rolling surface direction and the plate thickness direction. This causes the generation of fine openings in the plate thickness direction, called "separation", at a broken surface of the specimen when various toughness tests are performed using specimens taken in the rolling surface direction. In this way, the separation is caused by the large difference in toughness between the rolling surface direction and the plate thickness direction. Thus, the presence of sulfur (S) in the steel can also generate the separation, 25 in addition to the influence of the texture, because MnS is formed to extend in the rolling surface direction, mainly at a center segregation part located at the center of the steel in the thickness direction.

30 **[0005]** If the aforesaid separation occurs before a brittle crack is generated during the CTOD test, an opening might be judged wrongly to be stably formed only up to a position where the separation occurs. As a result, the critical CTOD value would be lower, compared to an intrinsic value. For this reason, in the material that causes such separation, for example, the improvement of the toughness of a base material alone that is assessed by a fracture transition temperature  $vT_r$ s cannot enhance the critical CTOD value.

35 **[0006]** This is why a steel plate required to ensure the adequate critical CTOD value is designed to ensure the target strength not to generate separation during rolling the steel plate, by using the solid solution strengthening by addition of expensive elements, or by complicated manufacturing steps incorporating a combination of a water-cooling equipment and a heating equipment on line, as disclosed, for example, in Patent Document 1.

**[0007]** Further, Patent Document 2 has proposed the application of special rolling conditions in which a steel plate is on standby while being air-cooled in rolling until its temperature decreases by 80°C or more in order to avoid the rolling in a temperature range that causes separation.

40 **[0008]** On the other hand, Patent Document 3 has proposed a technique that involves setting the upper limit of S content lower to decrease the amount of MnS formed, which would cause the separation, thereby suppressing the occurrence of separation.

**[0009]**

45 Patent Document 1: JP 2013-47393 A

Patent Document 2: JP 2003-96517 A

Patent Document 3: JP 2013-173998 A

50 **[0010]** The techniques disclosed in the above-mentioned Patent Documents 1 and 2 are very useful in enabling suppression of the occurrence of separation and increasing the critical CTOD value. However, these techniques require the solid solution strengthening by the addition of expensive elements, the complicated manufacturing steps incorporating the combination of the water-cooling equipment and heating equipment on line, and the adoption of the special rolling conditions, which inevitably leads to an increase in costs and a decrease in productivity.

55 **[0011]** The technique disclosed in the above-mentioned Patent Document 3 cannot eliminate MnS completely, which is not sufficient as a technique of suppressing the occurrence of separation. EP3018231 A1, EP2980238 A1 and JP2013213242 A disclosed a steel plate with excellent hydrogen-induced cracking resistance. JP2012072472 A and JP2003096517 A disclosed a steel plate for a high-strength line pipe.

[0012] The present invention has been made in view of the foregoing circumstances, and it is an object of the present invention to provide a steel plate for a high-strength line pipe with excellent low temperature toughness that can ensure the high critical CTOD value even when separation occurs, and can be easily manufactured at low cost, as well as a steel tube for a high-strength line pipe produced by using such a steel plate for a high-strength line pipe.

[0013] A steel plate for a high-strength line pipe according to the present invention that can solve the above-mentioned problems is defined in claim 1.

[0014] The present invention also includes a steel tube for a high-strength line pipe having excellent low temperature toughness manufactured by using the above-mentioned steel plate for a high-strength line pipe.

[0015] Accordingly, the present invention appropriately defines a chemical composition of the steel plate, and sets the average grain size of the steel plate in the t/4 position where t is the thickness of the steel plate as well as the separation index SI measured on the fracture surface of a Charpy specimen at a specified temperature, in respective appropriate ranges. With this arrangement, the present invention can achieve the steel plate for a high-strength line pipe that has excellent low temperature toughness and a tensile strength of 520 MPa or more and that can obtain the excellent critical CTOD value even when separation occurs in the CTOD test.

Brief Description of the Drawing

[0016] Fig. 1 is a schematic diagram of a fracture surface of a Charpy specimen for explaining a measurement method of a separation index SI.

[0017] The inventors have aimed to create a steel plate for a high-strength line pipe that can obtain the excellent critical CTOD value while allowing for the occurrence of separation to some extent without completely shutting out the occurrence of separation, and they have studied about the relationship between the occurrence of the separation in the CTOD test and the microstructure of the steel plate. As a result, the inventors have found out that the critical CTOD value measured in the CTOD test has a correlation with the separation index SI in the Charpy test, and that to ensure the excellent low-temperature toughness, ensuring the toughness of the steel plate as a base material by refining the grain is effective.

[0018] First, the requirements for specifying the steel plate for a line pipe according to the present invention will be described below.

(Average grain size in the t/4 position where t is a thickness of the steel plate: 10 μm or less)

[0019] In terms of ensuring the excellent low temperature toughness, it is necessary to attain the adequate toughness of a base material by refining the grains. To ensure the target low temperature toughness, the average grain size needs to be 10 μm or less in the t/4 position, which is the representative position for evaluating the steel plate properties. The average grain size is preferably 8.0 μm or less, and more preferably 7.0 μm or less. The smaller average grain size is better, but the lower limit of the grain size is approximately 4 μm or more.

(Separation index SI measured on fracture surface of Charpy specimen at a specified temperature: exceeding 0 mm/mm<sup>2</sup> and 0.30 mm/mm<sup>2</sup> or less)

[0020] The separation index SI of the fracture surface of the Charpy specimen of the steel plate at the specified temperature is set at 0.30 mm/mm<sup>2</sup> or less, thereby making it possible to ensure the target critical CTOD value even when separation occurs in the CTOD test. The target critical CTOD value is equal to or more than 0.15 mm when a testing temperature is set at -10°C. Note that the above-mentioned specified temperature can be determined from the following equation (1). That is, the testing temperature (specified temperature) for performing the Charpy test varies depending on the thickness of the steel plate. To evaluate the target critical CTOD value which is supposed at the testing temperature of -10°C, it is also necessary to consider this specified temperature (T<sub>1</sub>).

$$T_1 = T_2 - 6 \times (t)^{1/2} + 20 \quad (1)$$

where T<sub>1</sub> is a Charpy testing temperature (°C); T<sub>2</sub> is a CTOD testing temperature (°C), which is -10°C in the present specification; and t is a thickness (mm) of the steel plate.

[0021] As indicated by the equation (2) below, the separation index SI can be determined by dividing the total length of separations occurring in the direction perpendicular to the plate thickness direction on a fracture surface of the Charpy specimen by an area (cross-sectional area) of the fracture surface of the specimen (see Fig. 1 to be mentioned later).

$$SI = \Sigma(L_n) / S_A \quad (2)$$

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where  $L_n$  indicates a length (mm) of an n-th separation, and  $S_A$  is a cross-sectional area ( $\text{mm}^2$ ) of the fracture surface of the specimen.

**[0022]** In the steel plate for a high-strength line pipe according to the present invention, the separation index SI determined as mentioned above needs to be  $0.30 \text{ mm/mm}^2$  or less. The separation index SI is preferably  $0.20 \text{ mm/mm}^2$  or less, and more preferably  $0.15 \text{ mm/mm}^2$  or less. Note that from the purpose that even though separation occurs, the high critical CTOD value is exhibited, the separation index SI is not necessarily  $0 \text{ mm/mm}^2$ . In this regard, the separation index SI is preferably  $0.05 \text{ mm/mm}^2$  or more, and more preferably  $0.10 \text{ mm/mm}^2$  or more.

**[0023]** The chemical composition of the steel plate for a high-strength line pipe according to the present invention also needs to be adjusted as appropriate. The reason for setting the ranges of the respective chemical components in the composition will be mentioned below. Regarding the chemical composition, the term % as used herein means % by mass.

(C: 0.02 to 0.20%)

**[0024]** Carbon (C) is an element essential to ensure the strengths of a steel plate as a base material and a weld zone. To this end, the C content needs to be 0.02% or more. Further, the C content is preferably 0.03% or more, and more preferably 0.05% or more. Any excessive C content, however, is more likely to form a martensitic island (MA: Martensite-Austenite constituent), decreasing the toughness of a heat affected zone (HAZ) of the steel plate, and degrading the weldability. From this perspective, the C content needs to be 0.20% or less. Further, the C content is preferably 0.15% or less, and more preferably 0.12% or less.

(Si: 0.02 to 0.50%)

**[0025]** Silicon (Si) has a deoxidation function and is effective in improving the strength of the steel plate as the base material and a weld zone. To exhibit these effects, the Si content is set at 0.02% or more. The Si content is preferably 0.05% or more, and more preferably 0.15% or more. However, any excessive Si content degrades the weldability and toughness. Accordingly, the Si content needs to be suppressed to 0.50% or less. The Si content is preferably 0.45% or less, and more preferably 0.35% or less.

(Mn: more than 1.2% to 2.0%)

**[0026]** Manganese (Mn) is an element that is effective in improving the strengths of a steel plate as a base material and a weld zone. To exhibit these effects, the Mn content is more than 1.2%. However, any excessive Mn content not only promotes the occurrence of the separation because of the formation of MnS, but also degrades the HAZ toughness and weldability of the steel plate. Thus, the upper limit of the Mn content is set at 2.0% or less. The Mn content is preferably 1.9% or less and more preferably 1.8% or less.

(P: exceeding 0% and 0.010% or less)

**[0027]** Phosphorus (P) is an element inevitably contained in a steel plate. When the P content exceeds 0.02%, the base material toughness and the HAZ toughness of the steel plate are drastically degraded. In the present invention, the P content is 0.010% or less. The P content is preferably reduced as much as possible, but it is difficult to industrially set the P content at 0%.

(S: exceeding 0% and 0.01% or less)

**[0028]** Any excessive S content generates MnS, promoting the occurrence of separation. Thus, the upper limit of S content is set at 0.01% or less. The S content is preferably 0.008% or less, more preferably 0.0060% or less, and further preferably 0.0050% or less. In terms of suppressing the occurrence of the separation in this way, the S content is desirably set small, but it is difficult to industrially set the S content to less than 0.0001%. Thus, the lower limit of the S content is approximately 0.0001% or more.

(Al: 0.010 to 0.080%)

**[0029]** Aluminum (Al) is a strong deoxidation element. To obtain the deoxidation effect, the Al content needs to be 0.010% or more. Thus, the Al content is preferably 0.020% or more, and more preferably 0.030% or more. On the other hand, any excessive Al content forms a large amount of AlN to decrease the amount of TiN precipitates, degrading the HAZ toughness. Thus, the Al content needs to be 0.080% or less. The Al content is preferably 0.060% or less, and more preferably 0.050% or less.

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(Nb: 0.002 to 0.060%)

5 **[0030]** Niobium (Nb) is an element effective in enhancing the strength and the base material toughness of the steel plate without degrading its weldability. To exhibit such effects, the Nb content needs to be 0.002% or more. The Nb content is preferably 0.005% or more, and more preferably 0.010% or more. However, when the Nb content becomes excessive to exceed 0.060%, the toughness of the base material and HAZ is degraded. Thus, the upper limit of Nb content is set to 0.060% or less. The Nb content is preferably 0.050% or less, and more preferably 0.040% or less.

10 (Ti: 0.003 to 0.030%)

15 **[0031]** Titanium (Ti) precipitates as TiN in a steel. Thus, Ti is an element required to improve the base material toughness by the suppression of coarsening of austenite grains during heating of a slab and to improve the HAZ toughness by the coarsening of austenite grains in the HAZ during welding. To exhibit such effects, the Ti content needs to be 0.003% or more. The Ti content is preferably 0.005% or more, and more preferably 0.010% or more. On the other hand, any excessive Ti content degrades the base material and HAZ toughness, because of solute Ti and precipitated TiC. Thus, the Ti content needs to be 0.030% or less. The Ti content is preferably 0.025% or less, and more preferably 0.020% or less.

20 (Ca: 0.0003 to 0.0060%)

25 **[0032]** Calcium (Ca) serves to control the form of a sulfide and has an effect of suppressing the formation of MnS by forming CaS. To exhibit such an effect, the Ca content needs to be 0.0003% or more. The Ca content is preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, when the Ca content exceeds 0.0060% to become excessive, the toughness of the steel plate is degraded. Thus, the upper limit of the Ca content is 0.0060% or less. The Ca content is preferably 0.0050% or less, and more preferably 0.0040% or less.

(N: 0.0010 to 0.010%)

30 **[0033]** Nitrogen (N) precipitates as TiN in a steel. Thus, N is an element required to improve the base material toughness by the suppression of coarsening of austenite grains during heating of a slab and to improve the HAZ toughness by the coarsening of austenite grains in the HAZ during welding. To exhibit these effects, the N content is set at 0.0010% or more. The N content is preferably 0.0030% or more, and more preferably 0.0040% or more. Any excessive N content, however, degrades the HAZ toughness by the presence of the solid-solution N. Thus, the N content needs to be 0.010% or less. The N content is preferably 0.0080% or less, and more preferably 0.0060% or less.

35 (REM: 0.0001 to 0.0300%)

40 **[0034]** A rare earth element (REM) is an element effective in controlling the form of a sulfide and has an effect of suppressing the formation of MnS by forming REMS. To exhibit such effects, the REM content needs to be 0.0001% or more. The REM content is preferably 0.0003% or more, and more preferably 0.0005% or more. On the other hand, when REM is contained in a large amount, the effect is saturated. Thus, the upper limit of the REM content is 0.0300% or less. Note that in the present invention, REM means 15 lanthanoid elements from La to Lu, scandium Sc and yttrium Y.

45 (Zr: 0.0001 to 0.0200%)

50 **[0035]** Zirconium (Zr) contributes to improving the HAZ toughness by forming an oxide and dispersing it finely in the steel. To exhibit such an effect, the Zr content needs to be 0.0001% or more. The Zr content is preferably 0.0003% or more, and more preferably 0.0005% or more. On the other hand, any excessive Zr content forms coarse inclusions to degrade the base material toughness. Thus, the Zr content needs to be 0.0200% or less. The Zr content is preferably 0.0100% or less, and more preferably 0.0050% or less.

55 **[0036]** The chemical composition of the steel plate for a high-strength line pipe according to the present invention has been mentioned above in terms of its essential elements. The balance of the steel plate is substantially iron. As a matter of course, inevitable impurities are allowed to be brought and contained in the steel, depending on the situations, including raw materials, construction materials, facilities and the like. The above-mentioned inevitable impurities can include, for example, As, Sb, Sn, O, H and the like.

**[0037]** The steel plate for a line pipe according to the present invention also preferably further contains one or more elements selected from the group consisting of Cu, Ni, Cr, Mo and V in the following amounts as needed. The reasons for setting ranges when allowing the steel plate to contain these optional elements are as follows.

(Cu: exceeding 0% and 1.50% or less)

5 **[0038]** Copper (Cu) is an element effective in enhancing the strength of the steel plate. To exhibit such an effect, the Cu content needs to be 0.01% or more. The Cu content is more preferably 0.05% or more, and further preferably 0.10% or more. Any excessive Cu content, however, degrades the base material toughness. Thus, the Cu content is preferably set at 1.50% or less. The Cu content is more preferably 1.0% or less, and further preferably 0.50% or less.

(Ni: exceeding 0% and 1.50% or less)

10 **[0039]** Nickel (Ni) is an element effective in improving the strength and toughness of the base material and weld zone. To exhibit such effects, the Ni content needs to be 0.01% or more. Accordingly, the Ni content is more preferably 0.05% or more, and further preferably 0.10% or more. A large content of Ni, however, makes the structural steel plate extremely expensive. From the economic point of view, the Ni content is preferably 1.50% or less. The Ni content is more preferably 1.0% or less, and further preferably 0.50% or less.

15 (Cr: exceeding 0% and 1.50% or less)

20 **[0040]** Chrome (Cr) is an element effective in improving the strength of the steel plate. To obtain such an effect, the Cr content is preferably 0.01% or more. The Cr content is more preferably 0.05% or more, and further preferably 0.10% or more. On the other hand, when the Cr content exceeds 1.50%, the HAZ toughness of the steel plate is degraded. Thus, the Cr content is preferably 1.50% or less. The Cr content is more preferably 1.0% or less, and further preferably 0.50% or less.

25 (Mo: exceeding 0% and 1.50% or less)

30 **[0041]** Molybdenum (Mo) is an element effective in improving the strength and toughness of the base material. To exhibit such effects, the Mo content needs to be 0.01% or more. The Mo content is more preferably 0.05% or more, and further preferably 0.10% or more. However, when the Mo content exceeds 1.50%, the HAZ toughness and weldability of the steel plate are degraded. Thus, the Mo content is preferably 1.50% or less, more preferably 1.0% or less, and further preferably 0.50% or less.

(V: exceeding 0% and 0.1% or less)

35 **[0042]** Vanadium (V) is an element effective in improving the strength of the steel plate. To obtain such an effect, the V content is preferably 0.003% or more. The V content is more preferably 0.010% or more. On the other hand, when the V content exceeds 0.1%, the weldability of the steel plate and the base material toughness thereof are degraded. Thus, the V content is preferably 0.1% or less, and more preferably 0.08% or less.

**[0043]** Note that Cu, Ni, Cr, Mo and V are elements that improve the strength and toughness of the base material and the HAZ, and may be used individually, or alternatively two or more of these elements may be used together, as needed.

40 **[0044]** According to the present invention, the steel plate does not have the following composition in percent by mass: C: 0.07%, Si: 0.32%, Mn: 1.44%, P: 0.006%, S: 0.0009%, Al: 0.025%, Ca: 0.0036%, N: 0.0047%, O: 0.0021%, Ti: 0.011%, Cu: 0.15%, Ni: 0.23%, Cr: 0.26%, Mo: 0.09%, Nb: 0.010%, REM: 0.0021%, and Zr: 0.0011%, with the balance being iron and inevitable impurities.

45 **[0045]** In manufacturing the steel plate of the present invention, it is necessary to appropriately control manufacturing steps therefor. First, to control the form of a sulfide by REM and Ca, REM and Ca need to be added after the steel plate is deoxidized by Al and Zr, that is, after  $Al_2O_3$  and ZrO are formed by Al and Zr. Especially, Ca is apt to form an oxide. Ca is more likely to form an oxide (CaO) rather than a sulfide (CaS). To prevent the resulfurization from CaS, the time until the completion of casting is required to be restricted. Thus, when adding Al, Zr, REM and Ca in this order during a molten steel treatment step, a cast steel should be produced such that solidification is completed within 200 minutes after the addition of Ca. Further, the time from the sufficient formation of the REMS by the addition of REM to the addition of Ca, which has a higher sulfide formation capability than REM, should be four minutes or more. Through these steps, Ca and REM are present in the form of sulfides without forming any oxide.

50 **[0046]** For example, after producing the cast steel, such as a slab, in the way mentioned above, the slab is reheated at a heating temperature of 1,050 to 1,250°C, which is a normal temperature range, followed by a predetermined rough rolling. Subsequently, the rolled slab is hot-rolled in a temperature range of an  $Ar_3$  transformation point to 950°C (hereinafter referred to as an " $Ar_3$  point to 950°C") in such a manner that a cumulative rolling reduction ratio is 50% or more. By setting the cumulative rolling reduction ratio in the hot rolling at 50% or more, the average grain size of the steel plate can be 10  $\mu$ m or less in the t/4 position where t is the plate thickness of the steel plate. At this time, the cumulative rolling

reduction ratio is preferably 55% or more, and more preferably 60% or more. The upper limit of the cumulative rolling reduction ratio is approximately 80% or less in terms of actual operation.

**[0047]** Thereafter, another rolling process should be performed to ensure the cumulative rolling reduction ratio of 5% or more in the so-called dual-phase temperature range, which is a temperature range from ( $Ar_3$  transformation point - 60°C) to a  $Ar_3$  transformation point (which is hereinafter referred to as " $Ar_3$  point - 60°C to  $Ar_3$  point"). If the cumulative rolling reduction ratio at this time cannot be ensured to be 5% or more, the steel plate cannot attain the adequate strength. The cumulative rolling reduction ratio is preferably 10% or more, and more preferably 15% or more. When the cumulative rolling reduction ratio exceeds 35%, the texture is developed, resulting in an increase in the separation index SI. Thus, the cumulative rolling reduction ratio should be 35% or less. The cumulative rolling reduction ratio is preferably 30% or less, and more preferably 25% or less.

**[0048]** The above-mentioned term "cumulative rolling reduction ratio" means a value determined by calculation from the following equation (3). The above-mentioned temperature is defined as an average temperature determined by calculation from the surface temperature of the slab or steel plate, taking into consideration the plate thickness and the like.

$$\text{Cumulative Rolling Reduction Ratio} = (t_0 - t_1) / t_2 \times 100 \quad (3)$$

where in the equation (3) above,  $t_0$  is a rolling start thickness (mm) of the steel plate when the average temperature is within the rolling temperature range;  $t_1$  is a rolling end thickness (mm) of the steel plate when the average temperature is within the rolling temperature range; and  $t_2$  is a thickness of a cast piece (e.g., slab) before the rolling.

**[0049]** The above-mentioned  $Ar_3$  point for use is a point determined by the equation (4) below. The same goes for values shown in Table 2 as will be mentioned later.

$$Ar_3 \text{ (}^\circ\text{C)} = 910 - 310 \times [C] - 80 \times [Mn] - 20 \times [Cu] - 15 \times [Cr] - 55 \times [Ni] - 80 \times [Mo] + 0.35 \times (t - 8) \quad (4)$$

where in the equation (4) above, [C], [Mn], [Cu], [Cr], [Ni] and [Mo] indicate the contents (% by mass) of C, Mn, Cu, Cr, Ni and Mo, respectively, and  $t$  is a plate thickness (mm) when measuring the temperature.

**[0050]** The plate thickness of the steel plate for a high-strength line pipe according to the present invention is not specifically limited, but when using the steel plate as the material for the line pipe, the plate thickness is preferably at least 6 mm or more, and more preferably 10 mm or more. The upper limit of the plate thickness of the steel plate is preferably 30 mm or less, and more preferably 25 mm or less.

**[0051]** The steel plate for a high-strength line pipe according to the present invention is formed into a steel tube for a line pipe thereafter. The obtained steel tube reflects the properties of the steel plate as raw material and thus has excellent low temperature toughness.

#### Examples

**[0052]** The present invention will be specifically described below by way of Examples. The present invention is not limited to the following Examples.

**[0053]** Various steels (steels A to K) having the chemical compositions shown in Table 1 were manufactured (note that the symbol "-" in Table 1 means "not added".) At this time, in order to control the form of a sulfide, in the molten steel treatment step, the deoxidation was performed with Al and Zr, followed by the addition of REM and Ca to each steel. REM and Ca were added in this order. In this case, the time from the addition of REM to the addition of Ca was set at 4 minutes or more. After the addition of Ca, casting was started, whereby a slab of the steel was fabricated within 200 minutes after adding Ca. Note that REM was added in the form of misch metal containing La and Ce.

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[Table 1]

Steel Type	Chemical composition (% by mass) The balance being iron and inevitable impurities																
	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Mo	V	Nb	Ti	Ca	N	REM	Zr
A	0.07	0.30	1.75'	0.007	0.001	0.025	-	-	0.20	-	0.050	0.0301	0.012	0.0015	0.0045	0.0015	0.0008
B	0.10	0.30	1.55	0.010	0.002	0.025	-	-	-	0.04	0.060	0.030	0.015	0.0015	0.0045	0.0015	0.0005
C	0.07	0.30	1.55	0.007	0.001	0.025	-	0.25	0.25	-	0.045	0.030	0.012	0.0015	0.0045	0.0010	0.0005
D	0.10	0.25	1.60	0.010	0.005	0.025	-	-	-	-	-	0.015	0.007	0.0015	0.0030	0.0020	0.0010
E	0.07	0.30	1.55	0.007	0.001	0.025	-	-	0.30	-	-	0.030	0.012	0.0015	0.0045	0.0015	0.0005
F	0.08	0.30	1.55	0.007	0.002	0.025	-	0.80	-	-	-	0.030	0.012	0.0015	0.0045	0.0015	0.0005
G	0.04	0.30	1.90	0.007	0.002	0.030	0.40	0.40	-	-	-	0.035	0.012	0.0015	0.0040	0.0020	0.0020
H	0.08	0.25	1.60	0.010	0.005	0.025	-	-	-	0.20	-	0.015	0.012	0.0015	0.0045	0.0020	0.0010
I	0.04	0.30	2.20	0.010	0.007	0.025	-	-	-	-	0.035	0.025	0.012	0.0015	0.0045	0.0015	0.0005
J	0.09	0.30	1.70	0.030	0.002	0.025	-	-	0.10	-	-	0.030	0.012	0.0015	0.0045	0.0005	0.0005
K	0.07	0.30	1.60	0.010	0.015	0.025	-	-	0.20	-	0.050	0.015	0.012	0.0015	0.0045	0.0015	0.0005

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**[0054]** The obtained slab was reheated at a heating temperature of 1,080 to 1,180°C shown in Table 2, followed by the predetermined rough rolling. The rough-rolled steel was further hot-rolled at a cumulative rolling reduction ratio shown in Table 2 below at the temperature of Ar<sub>3</sub> point to 950°C. Subsequently, the hot-rolled steel was further rolled at a cumulative rolling reduction ratio shown in Table 2 below in the so-called dual-phase temperature range from (Ar<sub>3</sub> - 60°C) to Ar<sub>3</sub> point, and was then allowed to cool, thereby producing a steel plate of each steel. The rolling conditions are shown in Table 2 below together with the plate thickness t after the rolling, steel and Ar<sub>3</sub> point (samples No. 1 to 18).

[Table 2]

Test No.	Thickness t (mm)	Steel Type	Ar <sub>3</sub> point (°C)	Heating temperature (°C)	Cumulative rolling reduction ratio in a range of Ar <sub>3</sub> point to 950°C (%)	Cumulative rolling reduction ratio in a range of (Ar <sub>3</sub> point - 60°C) to Ar <sub>3</sub> point (%)
1	20	A	749	1,120	56	21
2	20	A	749	1,100	58	15
3	20	A	749	1,140	63	7
4	12	A	745	1,160	62	11
5	25	B	812	1,120	56	28
6	20	B	802	1,100	52	8
7	20	C	755	1,100	60	12
8	16	D	754	1,100	62	10
9	16	E	759	1,120	70	12
10	16	F	720	1,140	65	15
11	20	G	720	1,100	60	8
12	16	H	744	1,080	55	8
13	25	A	752	1,160	56	44
14	25	B	758	1,080	52	37
15	25	D	753	1,180	22	12
16	20	I	729	1,100	55	12
17	25	J	751	1,100	52	18
18	20	K	762	1,120	55	12

**[0055]** Regarding the obtained steel plate of each sample, an average grain size in the t/4 position where t is its thickness, tensile properties (yield stress, tensile strength), Charpy properties (separation index SI) and CTOD properties (critical CTOD value) were measured in the following ways,

(Measurement of Average Grain Size in t/4 Position)

**[0056]** A specimen of each sample was used in which its cross-sectional surface (L cross-sectional surface) perpendicular to the steel plate surface and in parallel with the rolling direction was polished and corroded with nital. The average ferrite grain size in each specimen was determined using an intercept method on photomicrographs that were taken at a magnification of 400x in the t/4 position as the measurement position where t is a thickness plate.

(Measurement of Tensile Properties (Yield Stress, Tensile Strength))

**[0057]** Regarding the tensile properties, an yield stress and a tensile strength of the respective samples were measured using a full thickness tensile specimen of each sample in conformity with API-5L standard by test methods based on the standard. In this way, the tensile properties of the samples were evaluated.

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(Measurement of Charpy Property (Separation Index SI))

5 **[0058]** A 2 mm V notched Charpy specimen of each sample in conformity with ASTM-A370 standard was used to evaluate the Charpy properties by a test method based on the standard. At this time, the Charpy specimen was taken from the  $t/4$  position of the sample where  $t$  is a thickness of the steel plate in such a manner as to be aligned with the direction of the CTOD specimen. Three tests were performed on the specimen at a specified temperature shown in Table 3 below to thereby measure separation indexes. The largest of the measured values was adopted as the separation index SI. Fig. 1 is a schematic diagram of a fracture surface of the Charpy specimen when measuring the separation index SI. Referring to Fig. 1, reference numeral 1 denotes a separation; 2 denotes a fracture surface; 3 denotes a 2 mm V notch; and 4 denotes the plate thickness direction. The separation index SI of each sample was determined by measuring lengths  $L_1$  to  $L_3$  of the separations generated at the fracture surface of the Charpy specimen of each sample and dividing the total length by the cross-sectional area of the fracture surface of the specimen according to the above equation (2).

15 (Measurement of CTOD Characteristic (Critical CTOD Value))

**[0059]** A three-point bending CTOD specimen with  $B \times 2B$  geometry of each sample in conformity with BS7448 standard was used to evaluate the CTOD properties by a test method based on the standard. The CTOD test was performed on two tests of each steel plate at  $-10^\circ\text{C}$ . One of them with the lower CTOD value was adopted as the critical CTOD value.

20 **[0060]** The above-mentioned results are shown in Table 3, together with the plate thickness  $t$  and the steel used.

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[Table 3]

Sample No.	Thickness t (mm)	Steel Type	Average grain size (µm)	Tensile properties		Charpy properties			CTOD properties	
				Yield stress (MPa)	Tensile strength (MPa)	Specific temperature (°C)	Separation index SI (mm/mm <sup>2</sup> )	Testing temperature (°C)	Critical CTOD value (mm)	
1	20	A	6.3	522	619	-17	0.238	-10	0.28	
2	20	A	6.1	519	615	-17	0.125	-10	0.40	
3	20	A	5.7	488	593	-17	0.088	-10	0.34	
4	12	A	5.3	512	634	-11	0.100	-10	0.91	
5	25	B	6.7	541	612	-20	0.275	-10	0.18	
6	20	B	7.2	452	550	-17	0.138	-10	0.41	
7	20	c	7.4	477	580	-17	0.088	-10	0.81	
8	16	D	8.6	440	547	-14	0.088	-10	0.51	
9	16	E	7.0	444	548	-14	0.088	-10	1.20	
10	16	F	7.2	462	571	-14	0.138	-10	0.33	
11	20	G	4.6	561	633	-17	0.100	-10	1.10	
12	16	H	7.0	511	591	-14	0.125	-10	0.66	
13	25	A	7.1	572	631	-20	0.375	-10	0.10	
14	25	B	7.6	555	609	-20	0.338	-10	0.12	
15	25	D	10.7	381	522	-20	0.125	-10	0.10	
16	20	I	7.2	510	642	-17	0.325	-10	0.12	
17	25	J	8.1	480	570	-20	0.213	-10	0.10	
18	20	K	7.7	499	587	-17	0.338	-10	0.13	

**[0061]** From these results, the following consideration can be made. Sample Nos. 1 to 12 satisfied all the chemical composition, the average grain size and the separation index SI specified by the present invention. It is found that the critical CTOD values of the sample Nos. 1 to 12 satisfied the target value range of 0.15 mm or more, even though separation occurred at the testing temperature of -10°C in the CTOD test.

**[0062]** In contrast, sample Nos. 13 to 18 did not satisfy at least one of the requirements defined by the present invention, and as a result, the critical CTOD values of these samples did not reach the target value. In the sample Nos. 13 and 14 among them, the cumulative rolling reduction ratios in the dual-phase temperature range became high, developing the textures, leading to large separation indexes SI. As a result, their critical CTOD values were small.

**[0063]** In the sample No. 15, the cumulative rolling reduction ratio in the range of Ar<sub>3</sub> point to 950°C became lower, increasing the average grain size to degrade the base material toughness. As a result, its critical CTOD value did not reach the target value. The sample No. 16 used the steel plate made of the steel I that contained Mn in an excessive amount by way of example. Thus, MnS was supposed to be formed in the center segregation part of the steel plate, leading to a large separation index SI. As a result, its critical CTOD value did not reach the target value.

**[0064]** The sample No. 17 used the steel plate made of the steel J that contained P in an excessive amount by way of example, which degraded its base material toughness. As a result, its critical CTOD value did not reach the target value. The sample No. 18 used the steel plate made of the steel K that contained S in an excessive amount by way of example. Thus, like the sample No. 16, MnS was supposed to be formed in the center segregation part of the steel plate, leading to a large separation index SI. As a result, its critical CTOD value did not reach the target value.

## Claims

1. A steel plate for a high-strength line pipe having excellent low temperature toughness, comprising, in percent by mass:

C: 0.02 to 0.20%,  
 Si: 0.02 to 0.50%,  
 Mn: more than 1.2% to 2.0%,  
 P: exceeding 0% and 0.010% or less,  
 S: exceeding 0% and 0.01% or less,  
 Al: 0.010 to 0.080%,  
 Nb: 0.002 to 0.060%,  
 Ti: 0.003 to 0.030%,  
 Ca: 0.0003 to 0.0060%,  
 N: 0.0010 to 0.010%,  
 REM: 0.0001 to 0.0300%, and  
 Zr: 0.0001 to 0.0200%,  
 optionally further comprising one or two or more elements selected from the group consisting of, in percent by mass:

Cu: exceeding 0% and 1.50% or less,  
 Ni: exceeding 0% and 1.50% or less,  
 Cr: exceeding 0% and 1.50% or less,  
 Mo: exceeding 0% and 1.50% or less, and  
 V: exceeding 0% and 0.1% or less,  
 with the balance being iron and inevitable impurities, wherein  
 an average grain size of the steel plate is 10 μm or less in a t/4 position where t is a thickness of the steel plate, and  
 a separation index SI measured on a fracture surface of a 2 mm V notched Charpy specimen of the steel plate in conformity with ASTM-A370 standard at a specified temperature exceeds 0 mm/mm<sup>2</sup> and is 0.30 mm/mm<sup>2</sup> or less,  
 wherein the steel plate does not have the following composition in percent by mass:  
 C: 0.07%, Si: 0.32%, Mn: 1.44%, P: 0.006%, S: 0.0009%, Al: 0.025%, Ca: 0.0036%, N: 0.0047%, O: 0.0021%, Ti: 0.011%, Cu: 0.15%, Ni: 0.23%, Cr: 0.26%, Mo: 0.09%, Nb: 0.010%, REM: 0.0021%, and Zr: 0.0011%, with the balance being iron and inevitable impurities.

2. A steel tube for a high-strength line pipe having excellent low temperature toughness, manufactured by using the steel plate for a high-strength line pipe according to claim 1.

**Patentansprüche**

1. Stahlblech für ein hochfestes Leitungsrohr mit hervorragender Tieftemperaturzähigkeit, umfassend, in Massenprozent:

5 C: 0,02 bis 0,20 %,  
 Si: 0,02 bis 0,50 %,  
 Mn: mehr als 1,2 % bis 2,0 %,
   
10 P: 0 % überschreitend und 0,010 % oder weniger,  
 S: 0 % überschreitend und 0,01 % oder weniger,  
 Al: 0,010 bis 0,080 %,
   
Nb: 0,002 bis 0,060 %,
   
Ti: 0,003 bis 0,030 %,
   
15 Ca: 0,0003 bis 0,0060 %,
   
N: 0,0010 bis 0,010 %,
   
REM: 0,0001 bis 0,0300 %, und
   
Zr: 0,0001 bis 0,0200 %,
   
gegebenenfalls weiter umfassend ein oder zwei oder mehrere Elemente, ausgewählt aus der Gruppe, bestehend
   
20 aus, in Massenprozent:

Cu: 0 % überschreitend und 1,50 % oder weniger,  
 Ni: 0 % überschreitend und 1,50 % oder weniger,  
 Cr: 0 % überschreitend und 1,50 % oder weniger,  
 Mo: 0 % überschreitend und 1,50 % oder weniger, und
   
25 V: 0 % überschreitend und 0,1 % oder weniger,  
 worin der Rest Eisen und unvermeidliche Verunreinigungen ist, wobei eine durchschnittliche Korngröße des Stahlblechs 10 µm oder weniger in einer t/4-Position beträgt, worin t eine Dicke des Stahlblechs ist, und ein Trennungsindex SI, gemessen auf einer Bruchoberfläche einer 2 mm V-gekerbten Charpy-Probe des Stahlblechs in Übereinstimmung mit Standard ASTM-A370 bei einer vorgegebenen Temperatur, 0 mm/mm<sup>2</sup> überschreitet und 0,30 mm/mm<sup>2</sup> oder weniger beträgt,
   
30 wobei das Stahlblech nicht die nachstehende Zusammensetzung in Massenprozent aufweist:  
 C: 0,07 %, Si: 0,32 %, Mn: 1,44 %, P: 0,006 %, S: 0,0009 %, Al: 0,025 %, Ca: 0,0036 %, N: 0,0047 %, O: 0,0021 %, Ti: 0,011 %, Cu: 0,15 %, Ni: 0,23 %, Cr: 0,26 %, Mo: 0,09 %, Nb: 0,010 %, REM: 0,0021 %, und  
 Zr: 0,0011 %, worin der Rest Eisen und unvermeidliche Verunreinigungen ist.

- 35 2. Stahlröhre für ein hochfestes Leitungsrohr mit hervorragender Tieftemperaturzähigkeit, hergestellt unter Verwendung des Stahlblechs für ein hochfestes Leitungsrohr nach Anspruch 1.

40 **Revendications**

1. Tôle d'acier pour un tuyau de canalisation à haute résistance ayant une excellente ténacité à basse température, comprenant, en pourcentage en masse :

45 C: 0,02 à 0,20%,  
 Si : 0,02 à 0,50%,  
 Mn : plus de 1,2 % à 2,0 %,
   
P : supérieur à 0 % et inférieur ou égal à 0,010 %,
   
S : supérieur à 0 % et inférieur ou égal à 0,01 %,
   
50 Al: 0,010 à 0,080 %,
   
Nb : 0,002 à 0,060 %,
   
Ti : 0,003 à 0,030 %,
   
Ca : 0,0003 à 0,0060 %,
   
N : 0,0010 à 0,010 %,
   
55 REM : 0,0001 à 0,0300 %, et
   
Zr : 0,0001 à 0,0200 %,
   
comprenant éventuellement en outre un ou deux éléments ou plus choisis dans le groupe constitué par, en pourcentage en masse :

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Cu: supérieur à 0 % et inférieur ou égal à 1,50 %,  
Ni : supérieur à 0 % et inférieur ou égal à 1,50 %,  
Cr: supérieur à 0 % et inférieur ou égal à 1,50 %,  
Mo : supérieur à 0 % et inférieur ou égal à 1,50 %, et

5 V : supérieur à 0 % et inférieur ou égal à 0,1 %, le reste étant du fer et des impuretés inévitables, dans lequel une taille moyenne de grain de la tôle d'acier est de 10  $\mu\text{m}$  ou moins dans une position t/4 où t est une épaisseur de la tôle d'acier, et  
10 un indice de séparation SI mesuré sur une surface de fracture d'une éprouvette Charpy entaillée de 2 mm V de la tôle d'acier conformément à la norme ASTM-A370 à une température spécifiée supérieure à 0 mm/mm<sup>2</sup> et inférieur ou égal à 0,30 mm/mm<sup>2</sup>, où la tôle d'acier n'a pas la composition suivante en pourcentage de la masse :  
15 C: 0,07 %, Si : 0,32 %, Mn : 1,44%, P: 0,006%, S : 0,0009%, Al : 0,025%, Ca : 0,0036%, N: 0,0047%, O: 0,0021%, Ti : 0,011%, Cu : 0,15%, Ni: 0,23%, Cr : 0,26%, Mo : 0,09%, Nb : 0,010%, REM: 0,0021%, et Zr: 0,0011%, le reste étant du fer et des impuretés inévitables.

2. Tube en acier pour un tuyau de canalisation à haute résistance ayant une excellente ténacité à basse température, fabriqué en utilisant la tôle d'acier pour un tuyau de canalisation à haute résistance selon la revendication 1.

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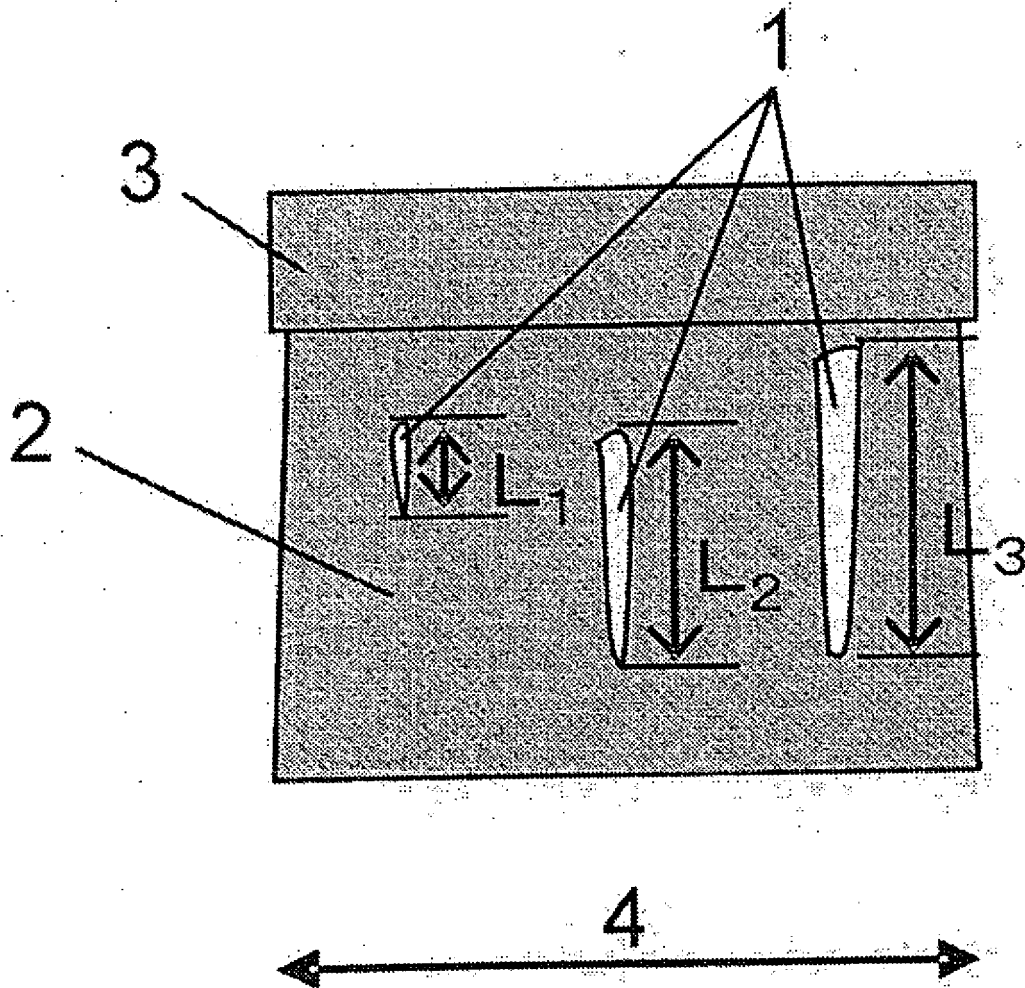
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[Fig. 1]



**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 2013047393 A [0009]
- JP 2003096517 A [0009] [0011]
- JP 2013173998 A [0009]
- EP 3018231 A1 [0011]
- EP 2980238 A1 [0011]
- JP 2013213242 A [0011]
- JP 2012072472 A [0011]